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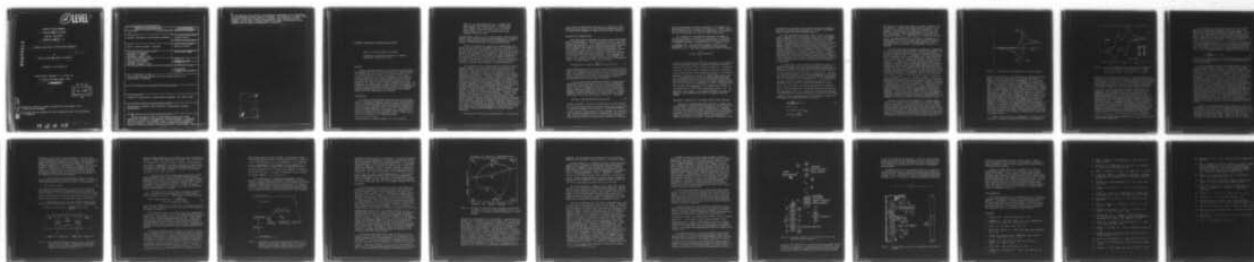
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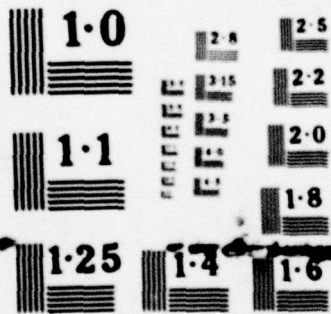
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and the importance and utility of electrochemical measurements in the preparation and understanding of these clusters is discussed. The preparation of mixed-valence polymers by solid-state reactions and by polymer growth techniques has been examined, and the types of behavior exhibited are shown to be explicable using arguments derived from the thermodynamics of solutions.

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## SYNTHETIC APPROACHES TO MIXED-VALENCE CHEMISTRY

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### ABSTRACT

Several preparative routes to mixed-valence materials have been examined and the effect of the synthetic variables discussed. It has been shown that solubility is a dominant factor in the successful isolation of many such materials. Soluble metal cluster complexes are susceptible to sequential oxidation/reduction reactions which lead to mixed-valence clusters, and the importance and utility of electrochemical measurements in the preparation and understanding of these clusters is discussed. The preparation of mixed-valence polymers by solid-state reactions and by polymer growth techniques has been examined, and the types of behavior exhibited are shown to be explicable using arguments derived from the thermodynamics of solutions.

### INTRODUCTION

The history of mixed-valence chemistry dates to the beginnings of coordination chemistry, since the first reported synthesis of a coordination compound involved a mixed-valence material. In 1704 Diesbach of Berlin, variously described as a chemist and an artist, prepared Prussian Blue by heating animal refuse and sodium carbonate together in an iron pot (1). A detailed preparation of Prussian Blue (2) and evidence demonstrating that it was an iron complex (3) were published in 1724. A short excerpt from that preparation (2) is reproduced below.

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\*Present address: Monsanto Company, St. Louis, Missouri.



Take 4 oz. of crude tartar and 4 oz. of dried crude nitre; powder them minutely and mix. Detonate them with charcoal, and you then have 4 oz. of extemporaneous alkali. While this salt is still hot it is finely powdered and 4 oz. of well-dried and finely powdered ox blood is added. . . .

Although modern synthetic work in mixed-valence chemistry rarely uses ox blood, the same basic process--serendipity or, depending on one's perspective, accident--is still responsible for the majority of the preparations of mixed-valence materials.

Because the ubiquity and importance of mixed-valence compounds were not generally recognized until 1967, when Robin and Day (4) and Hush (5) published their reviews of the area, it is not surprising that at that point there had been little systematic effort in the synthesis of such materials. Although this situation has changed in the past decade, few general treatments of the preparative aspects of mixed-valence chemistry have been published. Certain aspects of the field, such as the preparation of highly conducting one-dimensional solids and the design and synthesis of mixed-valence clusters, have been surveyed (6).

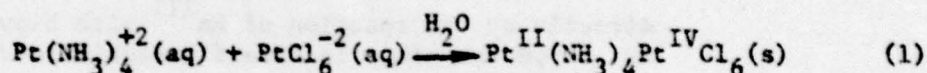
In this paper we hope to demonstrate that there are certain features common to the formation of stable or isolable mixed-valence compounds and that routes to such species need not be capricious. Our emphasis will not be so much on how to make particular compounds, but rather on the parameters which must be considered in the design of synthetic routes and on the competing reactions which may occur. A variety of factors, including the extent of interaction between adjacent sites, redox potential differences, solubility, and the availability of suitable precursors and oxidizing or reducing agents, dictate the success of an attempted preparation of a mixed-valence material, and the extent to which these factors can be controlled will be discussed. Following a brief discussion of systems where synthesis is either trivial or beyond the control of the synthesizer, we will concentrate on two types of mixed-valence material. First are those systems containing discrete molecular entities, clusters, where electrons can be added or subtracted sequentially and where, because solubility allows, the full range of synthetic techniques may be utilized. The second category includes polymeric systems which require incorporation of species of variable oxidation state within the growing polymer net or else solid-state transformations of a singly- to a mixed-valent species. The approach throughout this paper will be to seek generalizations which may prove to be useful while considering the synthesis of new mixed-valence materials.

We have made no effort to be comprehensive, or to survey the

entire field of mixed-valence synthesis, for indeed it is still true that there are nearly as many different preparative routes to mixed-valence compounds as there are mixed-valence compounds.

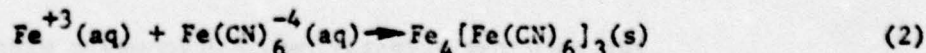
#### PREPARATION BY PRECIPITATION

Many mixed-valence compounds have been isolated only because, under the conditions of a particular reaction, they are the least soluble species present. In an equilibrium involving singly- and mixed-valent species, it is not necessary (for synthetic purposes) that the mixed-valence complex be the thermodynamically most stable material, e.g., that it dominate the equilibrium. Rather, if the proper conditions--such as solvent, temperature, and counterion--prevail, then the equilibrium may often be distorted by precipitation of the desired component. One consequence of this is that a virtually unlimited number of mixed-valence compounds could probably be prepared with relatively little synthetic effort. A simple example of this is shown in eq 1:



Mixing aqueous solutions of the Pt(II) cation and the Pt(IV) anion leads to the immediate precipitation of the mixed-valence product. There is no apparent interaction among the sites in this compound, and it is probable that the properties of most materials prepared in this fashion will be relatively uninteresting, typically exhibiting this Robin and Day Class I behavior.

Not all mixed-valence materials prepared by simple precipitation reactions are themselves trivial, and many demonstrate significant interactions among the ions of different oxidation state. This will in general be true if Lewis acid-base interactions among the components are possible, and is particularly probable if ligand-bridged metal ions can be formed. A notable example of this is the formation of Prussian Blue from aqueous solutions of ferric and ferrocyanide ions (eq 2). The cation

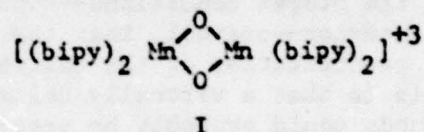


present,  $\text{Fe}(\text{H}_2\text{O})_6^{+3}$ , is labile to substitution, and hence behaves as a Lewis acid with respect to the Lewis base, the nitrogen atoms of the cyanide ligands in ferrocyanide. The resulting compound has  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  sites linked by cyanide bridges, and thus allows the intervalence transfer which is responsible for the characteristic color of Prussian Blue (7). As in the case of Prussian Blue, precipitation may be accompanied by substitution reactions,



and other coincident reactions are possible. For example, this same Prussian Blue may be prepared by reaction of aqueous ferrous and ferricyanide ions. In this case, precipitation is accompanied not only by substitution but also by valence interchange.

The complexity of the equilibria which may be present in solution, and hence the difficulty in predicting or controlling the ultimate products, is clearly demonstrated by the reactions of manganese acetates in the presence of 2,2'-bipyridine (bipy) or pyridine (py). The controlled oxidation of  $\text{Mn}^{\text{II}}(\text{OAc})_2$  by permanganate in the presence of bipy gives the mixed-valence  $\text{Mn}(\text{III},\text{IV})$  ion, I. This same bipyridyl(III,IV) dimer is produced



directly by the reaction of  $\text{Mn}^{\text{III}}$  with bipy at pH = 4.5. However, at low pH the dimer is itself unstable to disproportionation to  $[(\text{bipy})_2 \text{Mn}^{\text{III}}(\text{OH}_2)(\text{OH})]^{+2}$  and a  $\text{Mn}(\text{IV},\text{IV})$  dimer (8). In apparent contrast to this last result, reaction of bipy with the trimeric  $\mu_3$ -oxo-bridged  $\text{Mn}(\text{III})$  complex  $[\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{H}_2\text{O})_3]^+$  in methanol, followed by acidification, gives I in nearly quantitative yields (9). Although these results are not readily predictable, they are all compatible with a fairly facile oxidation of  $\text{Mn}(\text{III})$  to the mixed-valence  $\text{Mn}(\text{III},\text{IV})$  complex. The most surprising result, then, is that reaction of manganese(III) acetate,  $\text{Mn}(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_3$  with pyridine gives reduction to the trimeric mixed-valence  $\mu_3$ -oxo-bridged  $\text{Mn}(\text{II},\text{III},\text{III})$  complex  $\text{Mn}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{Py})_3$  (10). The apparently minor change of the ligands from bipy to py leads to seemingly very different stabilities for different oxidation states.

#### THE SOLUTION PREPARATION OF OLIGOMERIC MIXED-VALENCE COMPLEXES

Although the preceding examples would seem to suggest that the preparation of mixed-valence compounds is a rather arcane art, a large number of materials may be synthesized in a much more rational, and predictable, fashion. In particular, transformations involving soluble molecular species are not only frequently successful, but also offer great versatility in synthetic procedure, in architectural tinkering, and in the examination of chemical and physical properties. There has, consequently, been

a great deal of successful effort directed toward the synthesis and study of mixed-valence organometallic clusters, metal-metal bonded clusters, and ligand-bridged oligomers.

If the mixed-valence cluster is stable, soluble, and structurally comparable to a singly-valent analog, then its synthesis becomes relatively trivial, involving the selection of suitable solvents and chemical or electrochemical redox agents. Fortunately, the great activity in inorganic and, particularly, organometallic chemistry during the past 25 years has produced vast numbers of metal clusters which are potential precursors to mixed-valence compounds. The more fundamental problem in designing a synthesis using one of these precursors is whether the mixed-valence product will be a distinct, stable material. Its existence, compared to the fully oxidized or fully reduced species, is dependent upon its stability toward disproportionation, which in turn is dependent upon Coulombic effects involving the species as a whole and also upon the extent and nature of the interaction between sites.

For simplicity, we will consider a generalized cluster,  $M_2$ , containing two metal ions which are susceptible to oxidation. Removal of a single electron to form the mixed-valence cluster  $M_2^+$  occurs at potential  $E_1$  and removal of a second electron to form the fully-oxidized complex  $M_2^{+2}$  occurs at potential  $E_2$ . (Because our interest is primarily in potential differences, we will generally use thermodynamic standard potentials,  $E^\circ$ , and experimental half-wave potentials,  $E_{1/2}$ , interchangeably.) If the mixed-valence cluster is to be the dominant species at equilibrium, it is necessary that  $E_2$  occur at a more positive potential than  $E_1$  (e.g., that the standard electrode potential for the reduction  $M_2^{+2} + e^- \rightarrow M_2^+$  be larger than the standard electrode potential for the reduction  $M_2^+ + e^- \rightarrow M_2$ ). Under such conditions the equilibrium distribution of the various species is governed by the Nernst equation. Thus, the stability of the mixed-valence complex,  $M_2^+$ , with respect to disproportionation is given by:



$$E = E_1 - E_2$$

$$\Delta G = -nFE = -RT \ln K_{dis}$$

$$\log K_{dis} \approx \frac{E}{0.059}$$



The behavior of a particular system is strongly dependent upon the value of  $E$ . Because there has been much confusion on this problem in the past, we will discuss, in a general way, the behavior in three regimes, corresponding to  $E$  positive, near zero, and negative. The discussion here will be confined to symmetrical clusters,  $M_2$ , where there is no difference in metal sites. The same considerations will apply to unsymmetrical clusters  $MM'$  as well, but in those cases the innate preference for oxidation at a particular site will generally cause an intrinsic potential difference corresponding to the case of  $E$  negative.

On purely electrostatic grounds, a difference in potentials for the loss of the first and second electrons is expected, since the second electron leaves behind an ion of greater positive charge than does the first. In general, then, the mixed-valence state is expected to have some stability in clusters where both fully reduced and fully oxidized forms exist. Added stability may exist as a result of interaction between the sites within a cluster. In a mixed valence system with trapped valences  $(X,Y)$ , interaction with the valence interchange state  $(Y,X)$  provides a resonance or delocalization energy which stabilizes the mixed-valence state (11). The extent to which the excited state  $(Y,X)$  is mixed into the ground state  $(X,Y)$ , and hence the extent of the resonance stabilization, is dependent upon the existence of suitable orbital pathways. Consequently, systems like biferrocene and  $\{[(NH_3)_5Ru]_2(py_2z)}^{+5}$  ( $py_2z$  = pyrazine,  $C_4H_4N_2$ ), which have aromatic moieties connecting the metal ion sites, are reasonable candidates for stable mixed-valence systems. Indeed, for polyferrocenes each of the ferrocene centers is separately oxidizable to ferricinium at a distinct potential (12). Because the interaction between sites is potentially so strong, clusters with direct metal-metal interaction or with single-atom bridges are expected, and found, to yield a large number of mixed-valence materials. Thus, oxide-bridged clusters, such as the manganese-bipyridyl compounds discussed above and the  $\mu$ -oxo-tetraphenylporphinatoiron(III,IV) clusters prepared by Hendrickson (13), are examples of readily accessible, stable mixed-valence clusters.

Because the success of the synthesis of a mixed-valence cluster from a singly-valent precursor is so strongly dependent upon the potentials of the redox equilibria involved, electrochemical methods of investigation have been particularly useful. Electrochemical techniques have been widely used as both probes and preparative tools in mixed-valence cluster chemistry. Their utility arises because the potentials of electron transfer processes may be examined directly, providing information regarding the existence and stability of the mixed-valence clusters.

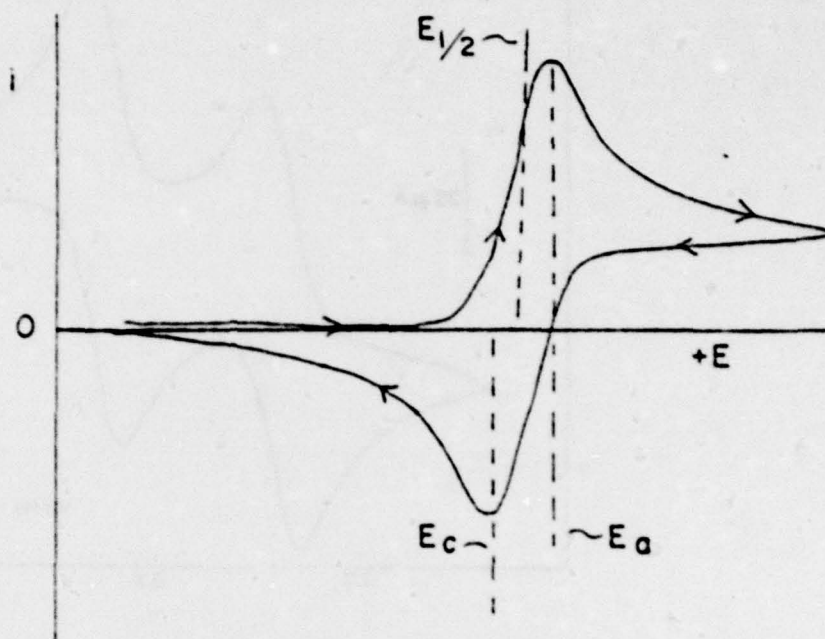


Figure 1. Typical cyclic voltammogram for a simple oxidation.

Although a great variety of electrochemical techniques are available, we will limit discussion here to cyclic voltammetry. Figure 1 shows a typical cyclic voltammogram (CV) for a simple oxidation. Over the course of the experiment the potential is swept in the direction indicated, first positive and then negative. In the case of a simple oxidation uncomplicated by preceding or succeeding chemistry, the current is controlled by a combination of thermodynamic (the Nernst equation) and kinetic (diffusion) factors. Although the mathematics leading to a curve of this shape can become rather complex, one feature of the curve is particularly important for our purposes. For a reversible, one-electron transfer, the peak-to-peak separation  $E_a - E_c$  is 60 mV. ( $E_a$  is the potential at the current maximum in the anodic, or oxidation, wave and  $E_c$  is the corresponding potential for the cathodic, or reduction, wave observed upon current reversal.) In general, for an  $n$ -electron transfer process the peak separation is  $60/n$  mV. Equivalent relationships involving  $n$ , the number of electrons transferred in a redox process, are available for many other electrochemical techniques. The implications of this relation with respect to the existence of mixed-valence species will be discussed below.

Figure 2 shows the cyclic voltammogram of biferrocene (12). There are two distinct one-electron processes, corresponding to



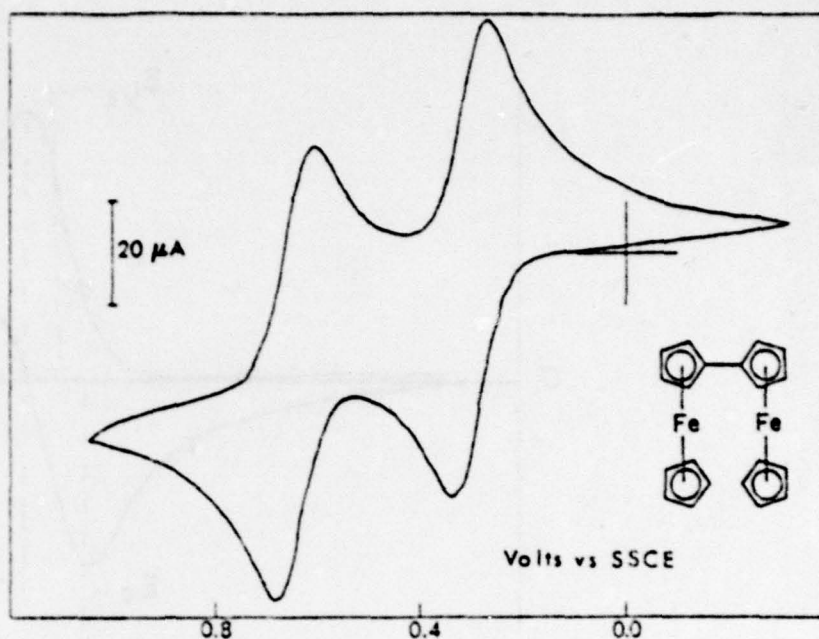
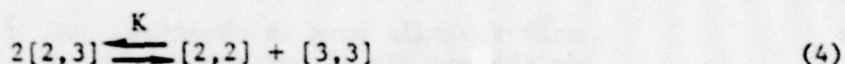


Figure 2. Cyclic voltammogram for the oxidation of biferrocene in 1:1 (v/v)  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{CN}$  containing 0.1 M. TBAH. Scan rate 200 mV/sec. (Courtesy of T. J. Meyer.)

oxidation of the ferrous compound [2,2] to the mixed-valence ion [2,3] and, at a more positive potential, oxidation of this species to the iron(III) complex [3,3]. The half-wave potentials of these two processes are 0.31 V and 0.65 V, respectively. As discussed previously, the equilibrium constant for the disproportionation of the mixed-valence ion can be calculated, and is found to be  $1.7 \times 10^{-6}$ . In this case, then, the mixed-valence state is a stable one, and its preparation is facile. In principle, its preparation may be affected using any oxidizing agent with a potential larger than that of the first wave (0.31 V here). If the oxidizing agent has a potential greater than that of the second wave, a stoichiometric amount must be added, otherwise an excess may be used. Of course, controlled potential electrolysis may also be used as a preparative technique. In the particular case of the biferrocene system, the mixed-valence complex has been prepared by oxidation with an excess of benzoquinone in the presence of picric acid (14). Direct synthetic advantage may be taken if the disproportionation equilibrium constant is small. Disproportionation of the Creutz and Taube ion,  $\{[(\text{NH}_3)_5\text{Ru}]_2(\text{pyz})\}^{+5}$ , has  $K_{\text{dis}}$  ca.  $10^{-6}$ , and the ion has been prepared by simply mixing stoichiometric quantities of the fully oxidized and fully reduced species (15).

As the strength of the interaction between sites becomes weaker, or as the distance between them becomes larger, the difference in electrode potentials will become smaller. In the limit of very large separation between sites, even the electrostatic contribution to the potential difference becomes negligible. Under these conditions, the isolation of the mixed-valence state becomes much more problematic. For example, the ion

$[(\text{bipy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{+2}$  ([2,2]) exhibits two one-electron cyclic voltammetry waves in which it is successively oxidized to the mixed-valence ion [2,3] and the fully oxidized [3,3] state (16). The potential difference for these two processes is only 0.12 V, and the disproportionation equilibrium (eq 4) has  $K = 0.01$ .

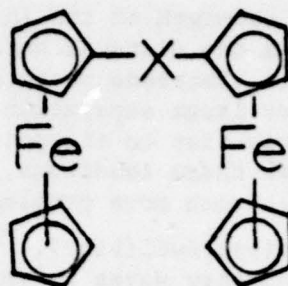


Although the mixed-valence ion is the dominant species, solutions of it at equilibrium contain ca. 10% of the fully oxidized and fully reduced forms.

As the interaction between sites becomes weaker still, the electrochemical behavior becomes more complex and the mixed-valence cluster ceases to dominate. For example, modifying the Creutz and Taube complex by substituting 4,4'-bipyridine in place of pyrazine leads to a cyclic voltammogram exhibiting one wave with a peak-to-peak separation of 114 mV. This was interpreted as being due to the superposition of two cyclic voltammetry waves separated by between 35 and 75 mV, corresponding to a fairly large disproportionation equilibrium (17). In the extreme of totally non-interacting centers, the microscopic redox potential for a given site is independent of the extent of oxidation of the other molecular sites, and the formal redox potentials and equilibrium constants are governed by statistical considerations. Recent theoretical treatment of this case has demonstrated that for non-interacting sites the cyclic voltammogram will have an identical shape to that of the corresponding species with only a single redox-active site (18). The curves will differ only in that the peak currents will be enhanced by the presence of multiple electroactive centers. As in the single-electron case, peak-to-peak separations should retain the theoretical limit of 60 mV.

A number of biferrocenes have been investigated using cyclic voltammetry, and the effect of bridging ligands upon the existence of discrete mixed-valence sites is clearly discernible (19). For species of the type II, separate one-electron waves are seen for the parent compound biferrocene and when X is small ( $\text{CH}_2$ ) or electronically delocalized ( $\text{C}\equiv\text{C}$ ). When X is large or unlikely to propagate an effective electronic interaction ( $X = \text{Hg}, \text{CH}_2\text{CH}_2$ )





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only a single wave is observed, with a peak current corresponding to the passage of two equivalents of electricity. Peak separations (and equivalent functions using other electrochemical techniques) were comparable for these systems and for ferrocene, demonstrating that two simultaneous one-electron processes, rather than a single two-electron process, were occurring. Similar behavior was observed in the electrochemistry of polyvinylferrocenes (18).

In these cases, where the difference in potentials for the two redox processes is zero, a statistical distribution of species prevails, and the equilibrium constant for disproportionation of the mixed-valence species is 0.25. This value arises because the mixed-valence ion has twice the probability of either of the two singly-valent species, analogous to the statistical factor in deprotonation of dicarboxylic acids. The important consequences of this value for the equilibrium constant have generally been overlooked. If one equivalent of oxidizing agent is added to a fully reduced two-metal cluster of this type, or if equal amounts of the fully reduced and fully oxidized forms are mixed, the resulting equilibrium mixture should contain the mixed-valence ion as the dominant (50%) species. Such a species should certainly be susceptible to spectroscopic characterization and may in fact be isolable. If a combination of solvent and counterion can be found with which the mixed-valence ion is the least soluble species, then in principle 100% yields of it may be attained. There have apparently been few attempts to isolate or examine mixed-valence complexes under such conditions. It should be emphasized, however, that the conclusion often reached--namely, that the observation of a single electrochemical wave implies that no stable mixed-valence species exists--is in general incorrect.

The final case to consider, and the sole exception to the last statement, is the case where  $E_2^0 < E_1^0$ . This implies that, in an oxidation, it is easier to remove the second electron than the first. This is clearly contrary to electrostatic predictions,

and can only occur if removal of the first electron leads to some electronic or molecular rearrangement which severely modifies the properties of the system. In such cases the disproportionation equilibrium is favored ( $K > 0.25$ ) and the mixed-valent species is a minor component of the equilibrium. As in the previous case, cyclic voltammetry will exhibit a single wave, but the peak-to-peak separation will be only 30 mV ( $=60/n$ ). It is this value which distinguishes a two-electron transfer from two simultaneous one-electron transfers. There are apparently few documented cases of this phenomenon. Fenton et al. (20) have recently reported the electrochemistry of a dicopper(II) macrocycle which undergoes two one-electron reductions with identical potentials (e.g.,  $E_2^\circ = E_1^\circ$ ). This implies a disproportionation equilibrium constant  $K = 1$ . Since this is larger than the statistical value of  $K = 0.25$ , it implies that the second electron is in fact easier (thermodynamically) to add than the first. Certain aryl substituted ethylenes exhibit a single two-electron oxidation wave, apparently as the result of the relief of steric strain by bond rotation following the initial oxidation (21).

Although this discussion has considered specifically only the ruthenium ammine dimers and the biferrocenes, it should be clear that the same considerations will apply to other soluble clusters. The synthesis of a mixed-valence cluster from its fully oxidized or reduced analog is primarily a matter of selecting suitable redox reagents and solvents.

#### THE PREPARATION OF POLYMERIC MIXED-VALENCE MATERIALS

Soluble mixed-valence complexes have a finite existence as distinct molecular, or ionic, entities. By contrast, the materials which will be discussed in this section exist only in the solid state. Dissolution, to the extent that it occurs, invariably involves either separation of the components of different formal oxidation state or redox processes which regenerate singly-valent species. Preparations of polymeric mixed-valence materials must then involve either solid-state reactions or polymer growth processes which incorporate the species of variable charge. Clearly, the precipitation reactions discussed above fall into this latter category. However, in many of the examples previously cited the driving force is the purely electrostatic interaction between, e.g., a Pt(II)-containing cation and a Pt(IV)-containing anion. In this section we will also consider the more complex cases--typified by  $K_2Pt(CN)_4Br_{0.3}$ --where ions of similar charge, but containing different oxidation states of a metal ion, aggregate through covalent bonding interactions.

A rather diverse group of mixed-valence materials may be



prepared by solid-state reaction techniques. Although solid-state syntheses are particularly applicable to the preparation of congruently-melting compounds such as bronzes, certain Magneli phases, mixed-valence perovskites and spinels, and vanadium-phosphate glasses, it is also possible to prepare, by solid-state reactions, mixed-valence coordination and organometallic complexes. It is instructive to list some conceivable synthetic techniques in order to gain an appreciation for the variety of processes occurring in the solid state which may be applied to the synthesis of mixed-valence compounds.

1. Binary or ternary transition-metal oxides or chalcogenides may be prepared by fusing together mixtures of upper- and lower-oxidation state compounds, as in eq 5. The facility of



this reaction is demonstrated by the fact that it occurs even when the solid reactants are separated by an ionic filter, as shown in Figure 3. Oxide transport through the ionic  $\text{ZrO}_2$  filter allows redox processes at both the  $\text{ZrO}_2/\text{FeO}$  and  $\text{ZrO}_2/\text{Fe}_2\text{O}_3$  interfaces, with formation of the mixed valence  $\text{Fe}_3\text{O}_4$  at each (22).

2. Thermal decomposition of singly-valent compounds often leads to mixed-valence species (23), as in eq 6. Occasionally,

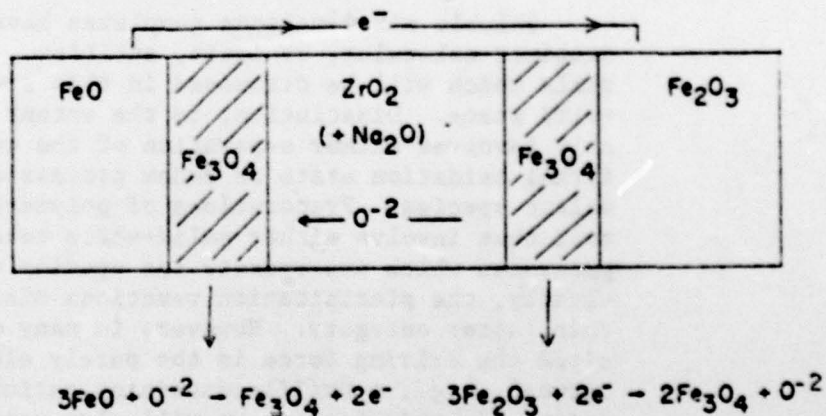
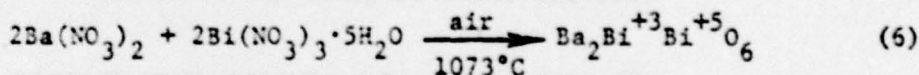
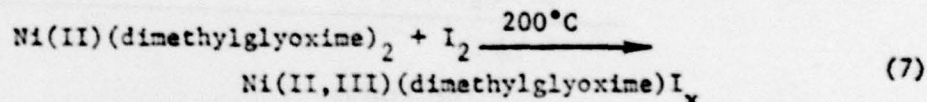


Figure 3. Solid state formation of  $\text{Fe}_3\text{O}_4$  by oxide ion transport through an ionic filter. Completing the electrochemical cell by connecting the  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  ends allows the reaction to continue (22).

partial thermal decomposition at ambient conditions can lead to a mixture of singly- and mixed-valent materials. Thus, the electrical conductivity of  $\text{Cs}_2\text{BaCo}^{\text{II}}(\text{NO}_2)_6$  is higher, by approximately five orders of magnitude, than that of analogs with other transition metals. This higher conductivity has been ascribed (24) to the generation of charge carriers by the solid state disproportionation of  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{I}}$  and  $\text{Co}^{\text{III}}$ .

3. Photolysis of solids (using either ultraviolet or high-energy radiation) often involves electron-transfer processes which generate different oxidation states of an element. Notable examples of this are the color centers in many minerals and the blue color (due to colloidal sodium) of rock salt (25). This is, in general, a non-equilibrium situation in which the kinetic barrier to recombination or reversal is so high that long-lived mixed-valence materials are formed.

4. The reaction of a singly-valent coordination compound with an oxidizing or reducing atmosphere can produce mixed-valence polymers, as in eq 7. These partial oxidation processes



have been used extensively in recent years, with activity in this area motivated largely by the current interest in the preparation of molecular metals (26).

The number and variety of materials which are, potentially, available by these routes is vast. Some useful preparative guidelines, based on the general reactions of solids, may be gleaned from several excellent monographs and texts (27). These references provide useful information on both theoretical (kinetic) and experimental (reactor design) considerations. They also are excellent sources for such germane topics as phase transformation kinetics and melting processes as well as gaseous diffusion into solids.

It should be emphasized that although the majority of solid-state syntheses of mixed-valence materials are based on stoichiometric considerations (i.e., eq 5), occasionally some surprising materials are obtained by attempting to synthesize mixed-valence compounds from "correct" (stoichiometric) mixtures of reactants. For example, although the Ba/Fe/S system contains a large number of compounds with "anticipated"  $\text{Fe}^{+2}/\text{Fe}^{+3}$  and  $\text{Fe}/\text{S}^{-2}$  ratios, two doubly-mixed-valence compounds  $\text{Ba}_4\text{Fe}_2\text{S}_6[\text{S}_{2/3}(\text{S}_2)_{1/3}]$  and  $\text{Ba}_{3.6}\text{Al}_{0.4}\text{Fe}_2\text{S}_6[\text{S}_{0.6}(\text{S}_2)_{0.4}]$  were prepared (28) by reacting BaS, Fe,



and S powders (and Al foils) at 1100°C. The presence of both sulfide and disulfide anions in these materials (as in Covellite, "CuS" =  $\text{Cu}_4^{+1}\text{Cu}_2^{+2}(\text{S}_2)_2\text{S}_2$ ) (29) is a reflection of the propensity of the chalcogenides to form oligomers at high temperature. On the other hand,  $\text{KCu}_4\text{S}_3$  has been shown by single-crystal x-ray analysis to contain only  $\text{S}^{-2}$  anions, which suggests the formulation  $\text{KCu}_3^{+1}\text{Cu}^{+2}\text{S}_3$  (30). Formation of polyanions is also observed in halogen chemistry, i.e.,  $\text{I}_3^-$ ,  $\text{I}_5^-$ , etc.

It is instructive to examine the thermodynamic factors involved in the existence of polymeric mixed-valence materials. Figure 4 contains a Born-Haber cycle for the formation of possible complexes between electron donor (D) and acceptor (A) molecules. Although as drawn Figure 4 is most appropriate for the consideration of organic complexes similar to those formed between tetrathiofulvalene (TTF) and tetracyanoquinodimethane (TCNQ), similar

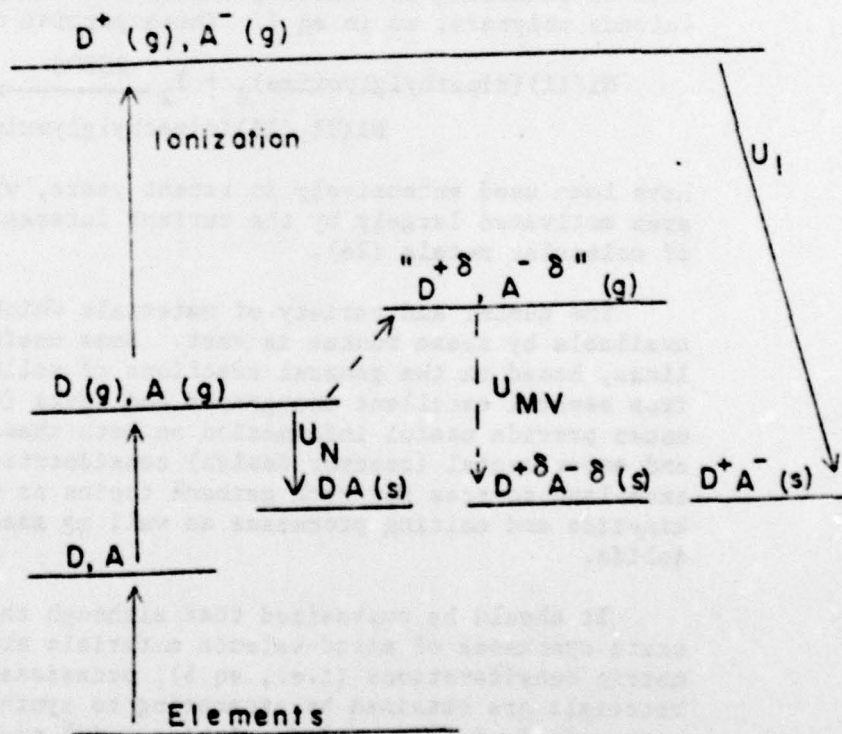


Figure 4. Born-Haber cycle for the interaction of donor (D) and acceptor (A) molecules. Calculations for the intermediate, mixed-valence complexes require formation of the imaginary, partially-ionized gaseous species.



cycles can be constructed for any material. The specific material which will form is determined by the relative magnitudes of the various ionization energies and binding energies,  $U$ . The ionization potential of  $D$  and the electron affinity of  $A$  (or quantities related to them) are, in general, measurable, and, in principle, the binding energies  $U$  can be calculated. However, unlike the simple ionic salts (e.g.,  $\text{NaCl}$ ) these calculations are distinctly non-trivial. The structures generally contain segregated stacks of  $D^{(+)}$  and  $A^{(-)}$ , rather than alternating ions, so that covalent bonding terms must be considered, and simplifying assumptions made in other cases are not valid here. Nonetheless, by accounting for a variety of steric and electronic factors, calculations of  $U_N$  and  $U_I$  have been made (31), which agree reasonably well with experiment.

In the discussion which follows, we will assume that it is possible to calculate the free energy (rather than the enthalpy) of formation for a donor-acceptor complex with any arbitrary degree of charge transfer, using thermochemical schemes conceptually similar to that in Figure 4. It might then be possible to calculate curves such as those shown in Figure 5, which show the variation in free energy of formation as a function of the degree of charge transfer. With some slight modifications these curves are also appropriate for exhibiting the variation in free energy of reaction as a function of the extent of partial oxidation of a metal complex by some external reagent. (For the purposes of illustration we have arbitrarily chosen the energy of the complete charge-transfer state,  $D^+A^-$ , to be higher than that of  $DA$ .) Assuming that there are no structural phase changes on proceeding from the neutral to ionic extremes (a surprisingly reasonable assumption (32) in the case of materials analogous to TTF-TCNQ), a smooth variation in energy results. We stress that our interest here is in the general behavior of materials in mixed-valence states, and that our attempt to fit all of these cases into the framework of a single diagram presents obvious problems in precision. Nonetheless, three types of energy variation, represented by curves 1, 2, and 3 in Figure 5, should be possible, corresponding to the cases where enthalpy terms are respectively unimportant, repulsive, and attractive.

It should be noted that these curves are similar to those observed for the free energy of solutions of two components, and indeed arguments from the thermodynamics of solutions are applicable here. In the case of the partial oxidation reaction, as in the ideal solution, the free energy will be decreased by entropic factors. Thus, each added ion ( $X^-$ ) can occupy a vast number of sites, and in so doing greatly increase the entropy of the system. Thus, in the case where no significant new enthalpy terms are

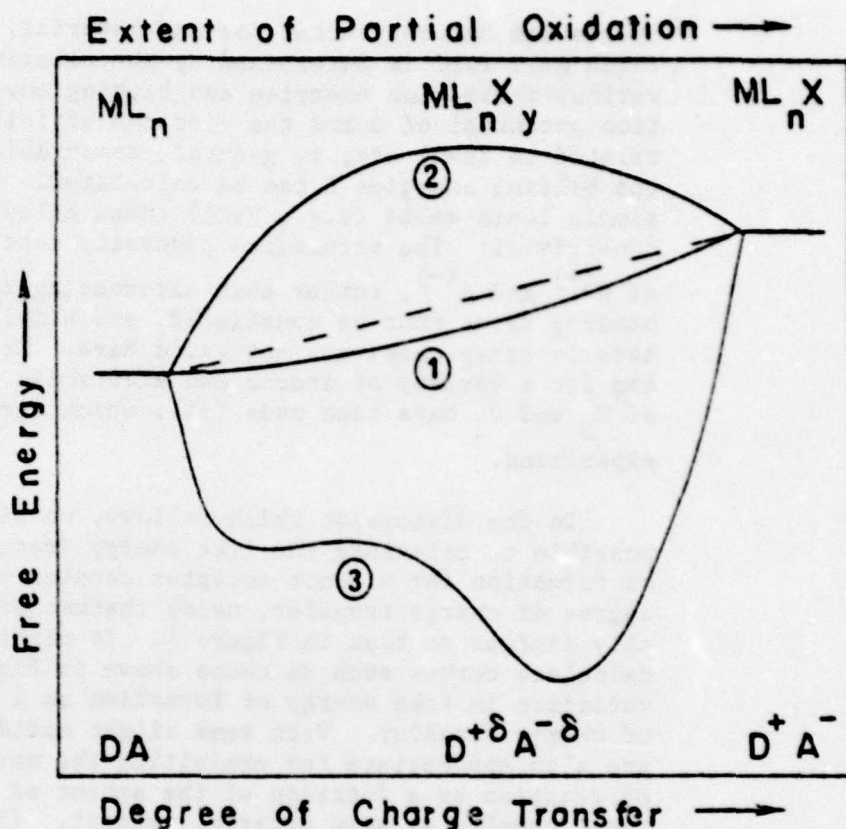


Figure 5. Variation in free energy as a function of the extent of charge transfer in a donor-acceptor complex or as a function of the degree of partial oxidation of a metal complex.

introduced, curves similar to 1 must prevail. Calculations show, however, that the entropy terms will be small, and that the overall behavior of a particular system is likely to be dominated by the enthalpy. Curve 1 represents the case where there is a monotonic increase in free energy as a function of the degree of intramolecular charge transfer. (For the ideal solution case, there should in fact be a shallow minimum near  $DA$ .) In the case of the donor-acceptor interaction this corresponds to the existence of a single stable form (the neutral compound as drawn here), and is certainly the most common situation. In the case of a partial oxidation reaction it corresponds to stoichiometric control, effectively the formation of a mixed-valence solid solution. This situation prevails, for example, in the doping of polyacetylenes with halogens (33). Thus, one can sequentially add iodine to solid  $(CH)_x$  with incorporation of variable amounts of I



dependent upon stoichiometry and conditions, and the physical properties of the product  $[(CH)I_y]_x$  vary in a continuous fashion.

Another example of this behavior involves a case where mixed-valence polymer formation is simultaneous with crystallization. Where typical geometries are the same for different oxidation states of an element, co-crystallization--in effect solid solution formation--is feasible. This is exemplified by the preparation of hexachloroantimonates (III,V). Compounds of general formula  $Cs_2Sb_y^{III}In_{1/2-y}^{III}Sb_{1/2}^{V}Cl_6$  were prepared by co-crystallization of the appropriate amounts of the singly-valent components. In this fashion, complexes can be prepared in which the ratio of  $Sb^{III}/Sb^{V}$  is continuously variable from 0/1 to 1/1 (34).

For the donor-acceptor complex, curves 1 and 2 both predict the same result, either no or complete charge transfer. However, for the partial oxidation reaction curve 2 corresponds to instability of the mixed valence phase. Stoichiometric control can no longer lead to a mixed-valence material, since if prepared it would be unstable with respect to disproportionation to the unoxidized and fully oxidized extremes. Synthetic efforts in such cases will go unrewarded, and probably unreported as well.

The most interesting case, of course, is represented by curve 3, since here the mixed-valence state is most stable. Predictions of the energy at intermediate states are quite difficult. There is, for example, the complication that structural parameters, and hence the various Coulombic terms, will vary with the degree of charge-transfer. This has been demonstrated in the case of KCP analogs, where the Pt-Pt separation is related to the formal oxidation state of the platinum (35). Although detailed calculations of the energy at intermediate degrees of charge transfer have not yet been successful, it is clear that a major factor will be the ease of charge transfer in the solid. This in turn must be related to other measures of electron transfer in donor and acceptor molecules. Working from this perspective, and utilizing solution redox potentials, Torrance has been quite successful in rationalizing and predicting which combinations of donor and acceptor organic molecules will give incomplete charge transfer and, consequently, high electrical conductivity (32). As in curve 3 in Figure 5, it is possible that several relative minima exist, which makes synthetic control a blend of thermodynamics and stoichiometry. This is exemplified by the partial oxidation of nickel complexes of 1,4,5,8,9,12,13,16-octamethyl-tetrabenzporphyrin (OMTBP).  $I_2$  oxidation of Ni(OMTBP) leads (36) to two distinct mixed valence phases, of composition Ni(OMTBP)( $I_3$ ) $_{0.35}$  and Ni(OMTBP)( $I_3$ ) $_{0.97}$ .



Because the nature of these curves can never be known in detail, they are in themselves of little direct synthetic utility. Nonetheless, knowledge of the possibilities can prove to be useful in designing syntheses, as has been demonstrated for the donor-acceptor complexes by Torrance (32). Similar predictive ability should exist for the partial oxidation reactions as well. Thus, precursors which have available structural sites that can accommodate oxidants with little distortion and with only minor enthalpy changes should exhibit behavior approaching that of the ideal solution. Consequently, curves of type 1, and a range of mixed valence materials dictated by stoichiometry, should result. Alternatively, curves of type 2 or 3 are more likely if either the nature of the oxidant or structural considerations lead to some specific interaction between the complex and oxidant. Depending on the bonding or antibonding nature of that interaction--which may be predictable--the mixed-valence state will be either stabilized or destabilized.

It should be emphasized that in all of these cases, kinetic factors can obviate any generalizations based on thermodynamic factors. This is particularly important for reactions involving solids, because of the low reactant mobility in the solid state. Thus, many thermodynamically non-viable mixed-valence materials have undoubtedly been prepared, and, similarly, many potentially stable mixed-valence compounds are simply inaccessible because of synthetic (kinetic) limitations.

Preparative methods involving partial oxidation and subsequent crystallization have been particularly useful in preparing highly-conducting one-dimensional metal complexes such as KCP. The most convenient chemical preparation of this compound involves mixing aqueous solutions of  $\text{K}_2\text{Pt}(\text{CN})_4$  and  $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_2$  (or, equivalently, adding a sub-stoichiometric amount of  $\text{Br}_2$  to aqueous  $\text{K}_2\text{Pt}(\text{CN})_4$ ). In this case the least soluble component is the mixed-valence KCP. Figure 6 demonstrates some of the chemical processes which are involved in a reaction such as the formation of KCP. It is clear that, given the large number of possibilities, it is fortunate that thermodynamics favors the mixed-valence compound here.

As a point of interest, it may be somewhat surprising that it is sometimes difficult to distinguish between single (homogeneous) phase and truly multiple (heterogeneous) phase syntheses of mixed-valence materials. For example, the partial oxidation of many "insoluble" stacked, square-planar  $d^8$  transition-metal complexes may be accomplished by slurrying the singly-valent compound in a solution of an oxidizing agent in an inert solvent. Although the reaction may in fact be heterogeneous, involving the

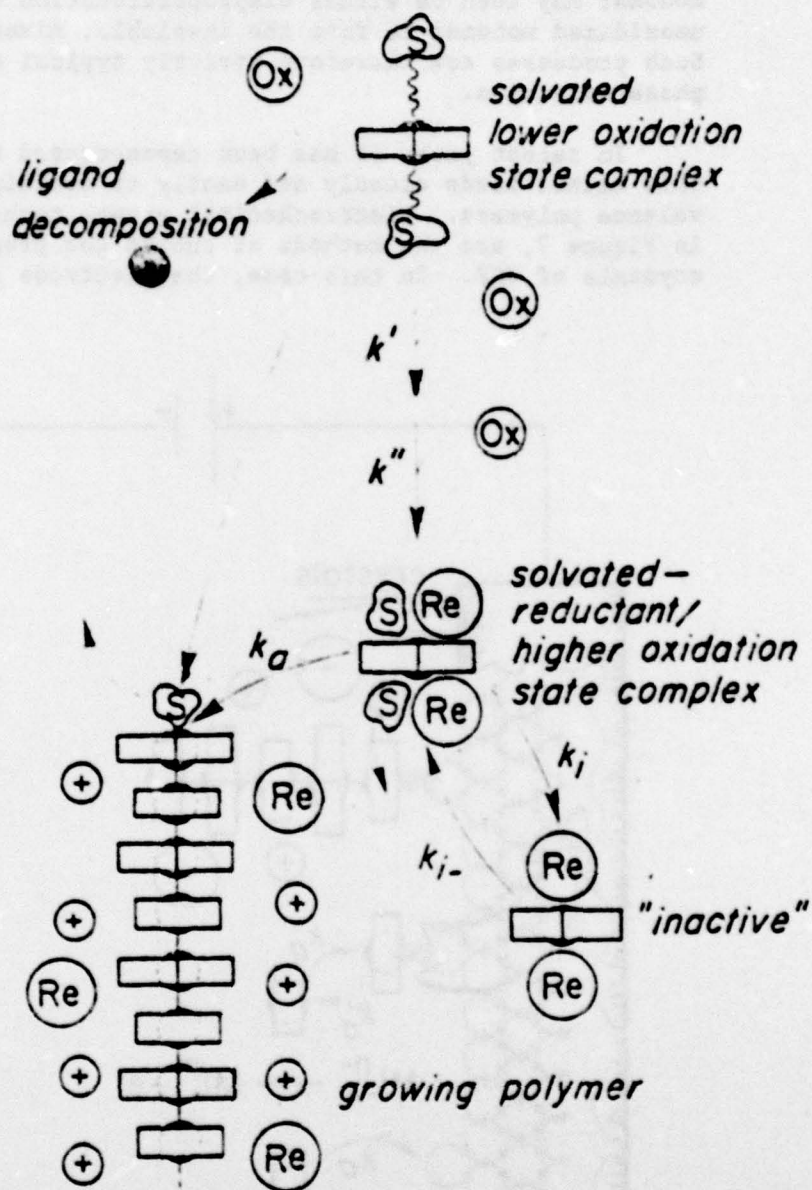


Figure 6. Processes involved in the formation of KCP by the partial oxidation reaction.

complex as the solid only, it is likely that in many cases product formation is the result of a complex series of equilibria. Thus, the reaction sequence may involve dissolution of the (insoluble) polymer into (soluble) monomers which are then rapidly oxidized



by the solution-phase oxidizing agent. The fate of the oxidized monomer may then be either disproportionation or combination with unoxidized monomer to form the insoluble, mixed-valence polymer. Such processes are therefore strictly typical of a homogeneous-phase oxidation.

In recent years it has been demonstrated that a variation of this method leads cleanly and easily to certain conducting mixed-valence polymers. Electrochemical growth techniques, illustrated in Figure 7, are the methods of choice for preparing large single crystals of KCP. In this case, the electrode serves as both the

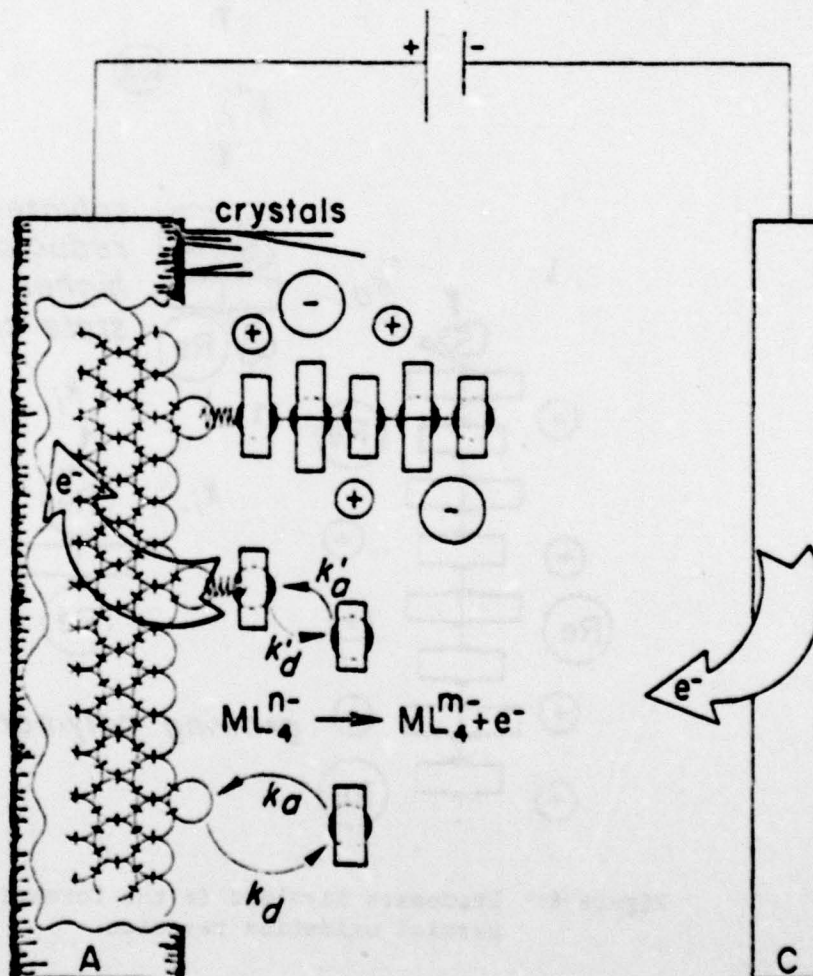


Figure 7. Electrochemical growth of a conducting, mixed-valence polymer.



oxidant and the nucleation site for crystal growth. Clearly, crystalline material will form only if the product is electronically conducting, since only then can electrons migrate from the crystal/solution interface.

Finally, it seems appropriate to emphasize that not all mixed-valence compounds need to be synthesized, since some are naturally occurring. A great number of mixed-valence minerals are known, most presumably forming during the slow crystallization processes which led to the formation of the earth's crust. Mixed-valence compounds are also formed in biological systems. Included here are the non-heme iron proteins which exhibit such a rich redox chemistry, and also the several animals--homing pigeons, honey bees, spirillum bacteria--which appear to possess a magnetic sense of direction as a result of their growth of single-domain crystals of magnetite,  $\text{Fe}_3\text{O}_4$  (37).

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